

# Layered Cathode Materials



*... for a brighter future*

presented by

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Annual Merit Review

DOE Vehicle Technologies Program

Washington, D.C.

May 21, 2009



U.S. Department  
of Energy

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***Vehicle Technologies Program***



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# Overview

## Timeline

- Start date: FY08
- End date: On-going
- Percent complete:
  - project on-going

## Budget

- Total project funding
  - 100% DOE
- FY08: \$300K
- FY09: \$300K
- FY10: \$400K

## Barriers Addressed

- Low energy
- Cost
- Abuse tolerance limitations

## Partners

- Co-investigators:
  - S.-H. Kang, C. Lopez Rivera, R. Benedek, C. Johnson (Argonne)
- Collaborators:
  - C. Grey, J. Cabana (SUNY – SB)
  - X.-Q. Yang (BNL)
  - C. Wolverton, D. Shin (NU)
  - Primet Precision Materials

# Objectives

- Design high capacity, high-power and low cost cathodes for PHEVs and EVs
  - *Improve the design, composition and performance of Mn-based cathodes*
  - *Use theoretical modeling as a guide to identify, design and understand the electrochemical properties of novel cathode structures*

# Milestones (FY08-09)

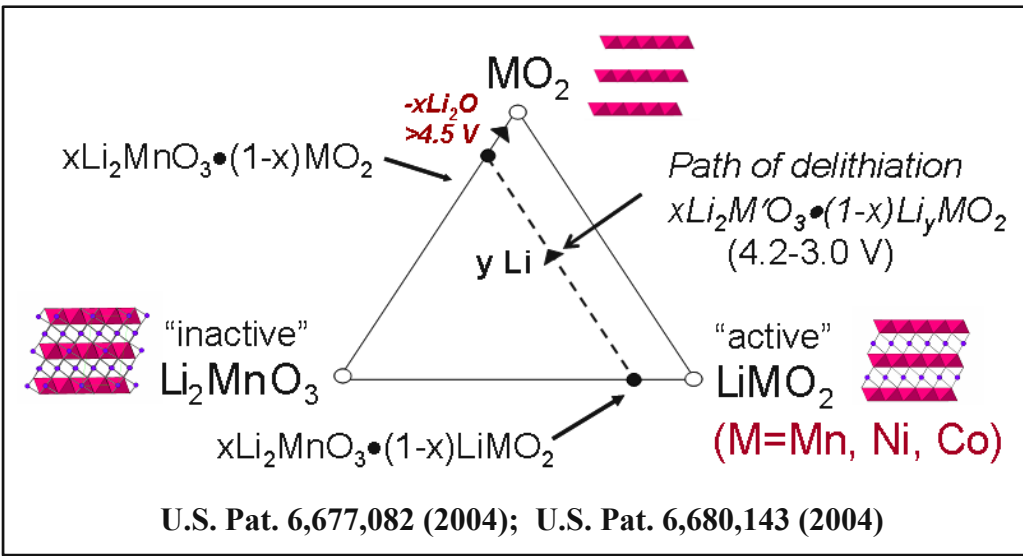
- Synthesize, evaluate and optimize high capacity Mn-based cathodes ( $>200$  mAh/g,  $>3$  V) – *on going*
- Enhance surface and cycling stability at high potentials ( $>4.2$  V) – *on going*
- Model interfacial structures and dissolution phenomena – *on going*
- Determine electrochemical properties of blended  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$  and spinel electrodes – *on going*
- Explore new materials and processes, including phosphates – *on going*

# Approach

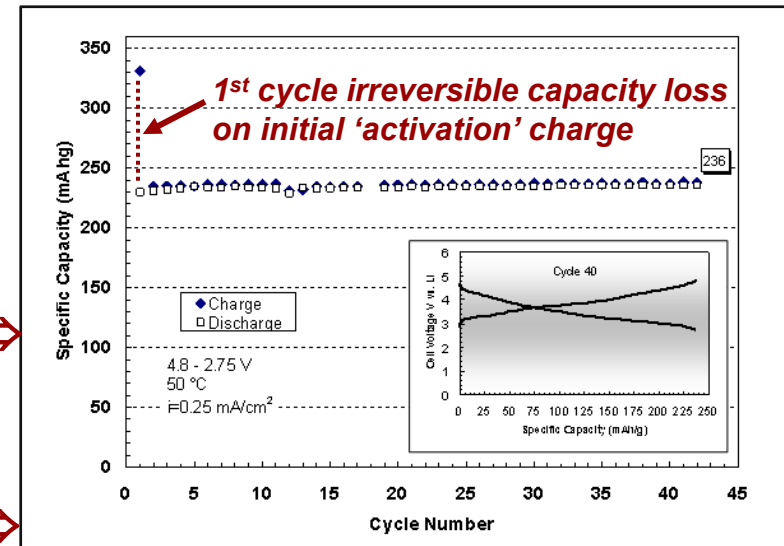
- Exploit the concept and optimize the performance of structurally-integrated, high-capacity electrodes such as 'layered-layered'  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$  ( $\text{M}=\text{Mn}, \text{Ni}, \text{Co}$ ) and 'layered-spinel'  $y[x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2] \bullet (1-y)\text{Li}_{1+z}\text{Mn}_{2-z}\text{O}_4$  electrodes.
- Extend the concept of using integrated bulk electrode structures to surface structures that protect the underlying metal oxide particles from the electrolyte, when charged (delithiated) at high potentials.
- Use computational modeling to aid the design of bulk and surface cathode structures and to understand electrochemical properties

# $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ Electrodes (Recap)

- **Strategy:** Embed inactive  $\text{Li}_2\text{MnO}_3$  component within  $\text{LiMO}_2$  structure to stabilize the electrode at high potentials (reduce oxygen activity at surface)



⇒ Keep  $\text{Li}_2\text{MnO}_3$  content as low as possible to maximize capacity



200-250 mAh/g achievable from high Mn-content electrodes at C/3 rate (50 °C)

**Disadvantage: Lower capacity at RT**

Large irreversible capacity loss on initial cycle ( $\text{Li}_2\text{O}$  removal from  $\text{Li}_2\text{MnO}_3$ )

# The Challenge of Surface Stabilization

- Charging high-capacity  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  electrodes to a high potential ( $>4.4$  V) damages the electrode surface and reduces the rate capability of the electrode:



- Oxygen loss, particularly through process (1), increases M cation concentration at the electrode surface that restricts Li diffusion and rate capability?



- *How does one prevent corrosion and cation disorder at the surface to allow high rate discharge and charge?*

# Fluoride- vs. Phosphate Stabilized Surfaces

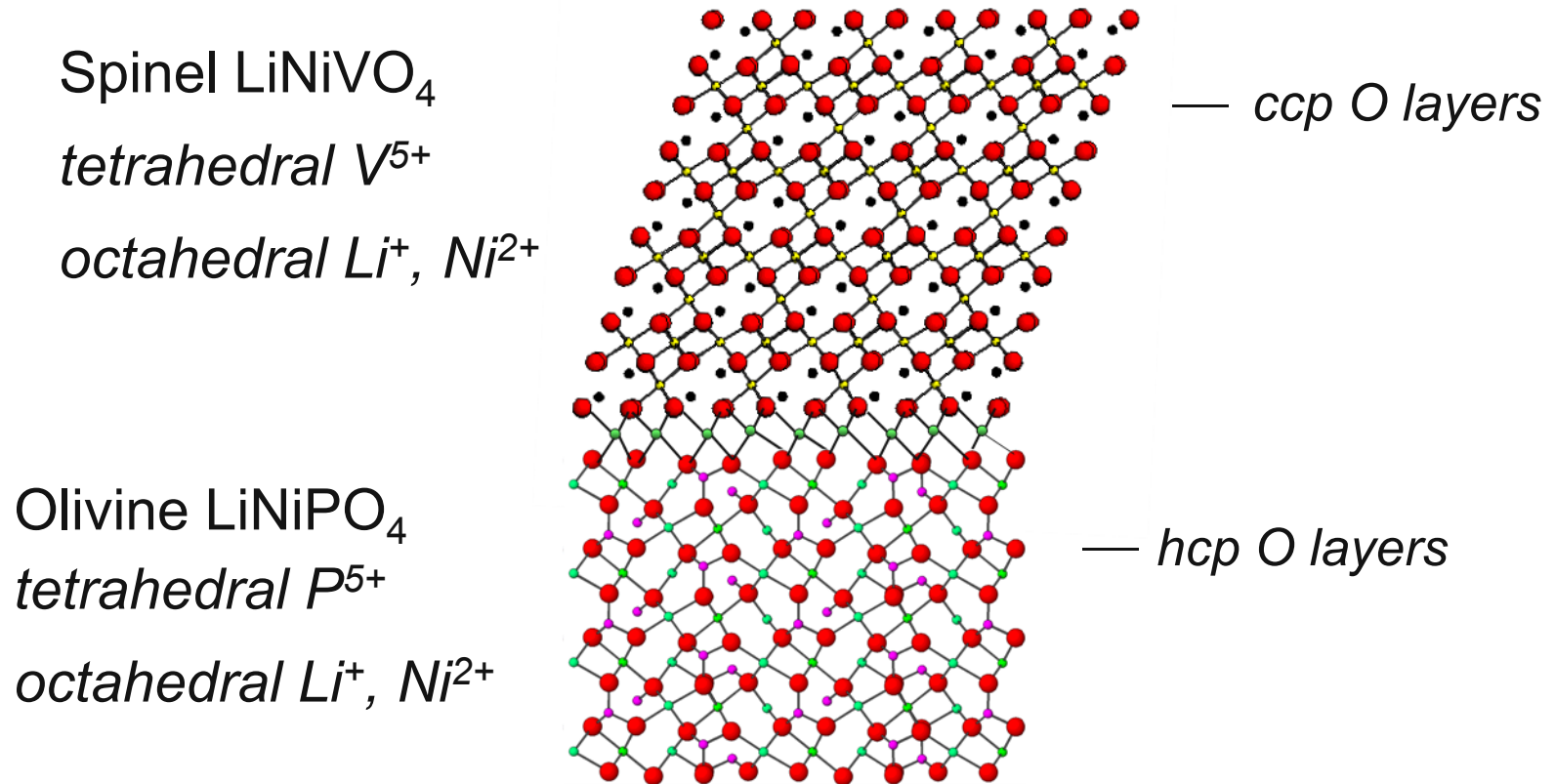
- Fluorination of layered  $\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$  and  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$  electrodes improves cycling stability and rate, notably at 50 °C (Sun, Amine)
- $\text{F}^-$  ions within the bulk or at the surface?
- Fluorination with mildly acidic solutions ( $\sim 2.5 \times 10^{-3} \text{ M}$ ;  $\text{pH} \approx 6.0 - 6.5$ ) stabilizes electrode surface at 4.6 V and improves rate capability (BATT Review 2008).
- $\text{AlPO}_4$  coatings improve cycling stability of  $\text{LiCoO}_2$  and  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$  electrodes (Cho, Manthiram)
- *Improvement in the rate capability of  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$  high-capacity electrodes particularly at room temperature is still required to meet the 40-mile range battery requirement for PHEVs.*
- $\text{Li-M-PO}_4$  stabilized surfaces? – New work – 2008/2009



# Integrated Olivine-Spinel Structures/Surfaces?

- Olivine ( $\text{LiFePO}_4$ ) and Spinel ( $\text{LiMn}_2\text{O}_4$ ) both have  $\text{AB}_2\text{O}_4$  formulae with the A cations in tetrahedral sites and the B cations in octahedral sites
- In  $\text{LiFePO}_4$ , the P cations are in tetrahedral sites
- In  $\text{LiMn}_2\text{O}_4$ , the Li cations are in tetrahedral sites
- Olivine has a hexagonally close packed structure
- Spinel has a cubic close packed structure
- Relatively small difference in the d-spacings of the close-packed layers in  $\text{LiFePO}_4$  and  $\text{LiMn}_2\text{O}_4$ 
  - Can we synthesize ‘olivine-spinel’ composite structures, ‘olivine-layered’ structures or other close-packed phosphate structures to stabilize spinel and layered metal oxide bulk structures and/or surfaces?

# Hypothetical $\text{LiNiVO}_4$ Spinel – $\text{LiNiPO}_4$ Olivine Intergrowth

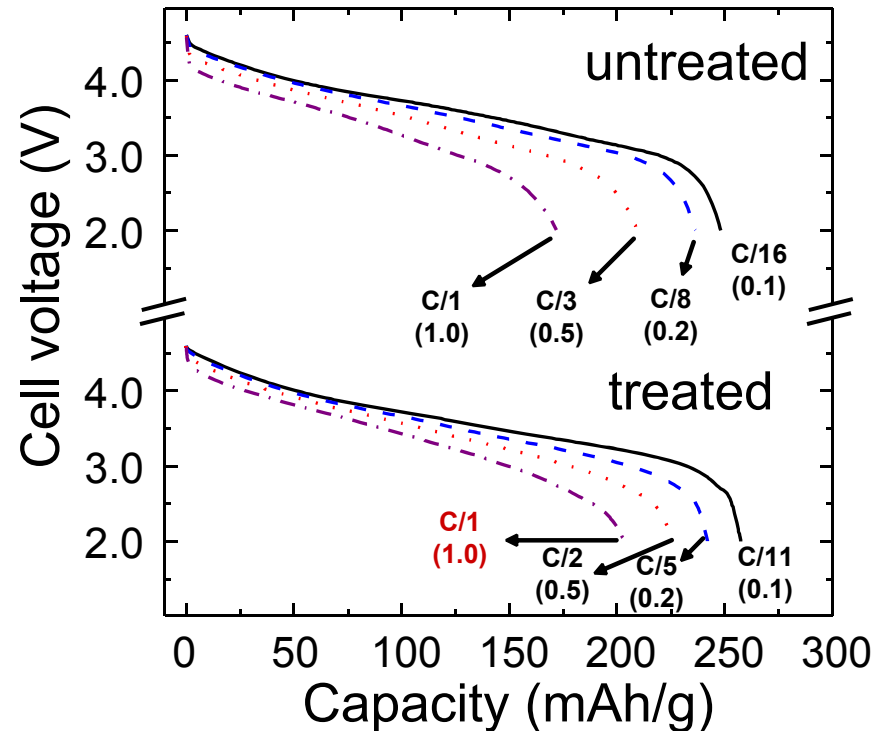


- In principle, a spinel-olivine intergrowth structure seems possible
- Experiment shows otherwise: CBED patterns and EDS signals ( $\text{Ni/V}$  or  $\text{Ni/P}$ ) suggest that discrete olivine and spinel phases exist
- Can  $\text{Li-M-PO}_4$  films provide effective surface protection on metal oxides?

# Li-M-PO<sub>4</sub> surface treatment (e.g., M=Ni)

(0.5Li<sub>2</sub>MnO<sub>3</sub>•0.5LiNi<sub>0.44</sub>Co<sub>0.25</sub>Mn<sub>0.31</sub>O<sub>2</sub> electrodes in Li half cells)

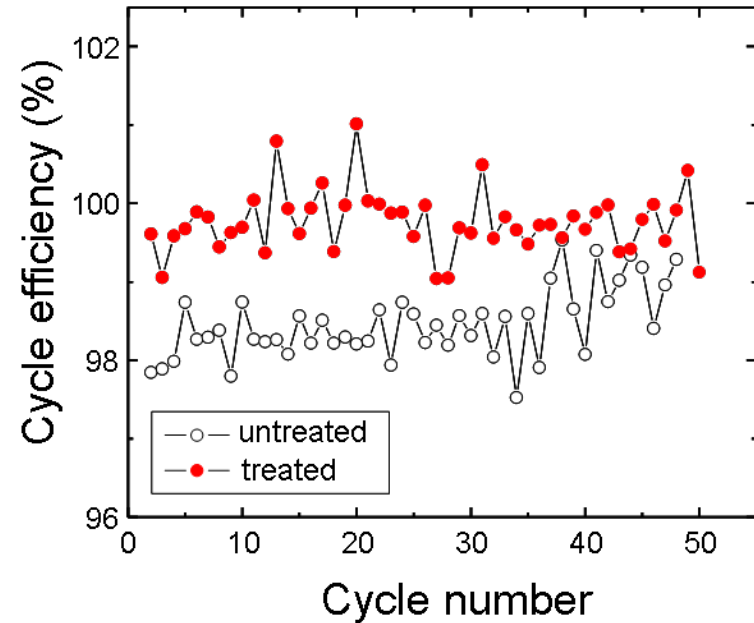
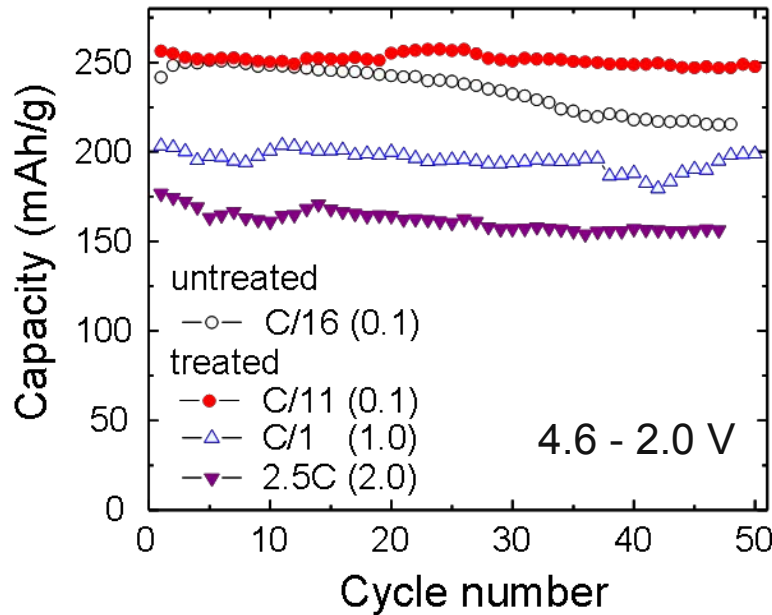
- Concept: Use Li-Ni-PO<sub>4</sub> as a solid electrolyte below 5.0 V to protect surface of xLi<sub>2</sub>MnO<sub>3</sub>•(1-x)LiMO<sub>2</sub> electrode at high potentials
- Sol-gel treatment technique used
- Olivine LiNiPO<sub>4</sub> or defect Li<sub>3</sub>PO<sub>4</sub>, e.g., Li<sub>3-2x</sub>Ni<sub>x</sub>PO<sub>4</sub>?
- Theoretical modeling of surface structures initiated (Shin, Wolverton)



Treated electrodes meet the 200 mAh/g, C/1 rate, 3.5 V average, capacity/power yardstick for a 40-mile range PHEV at room temperature

# Cycling Stability at Various C Rates (mA/cm<sup>2</sup>)

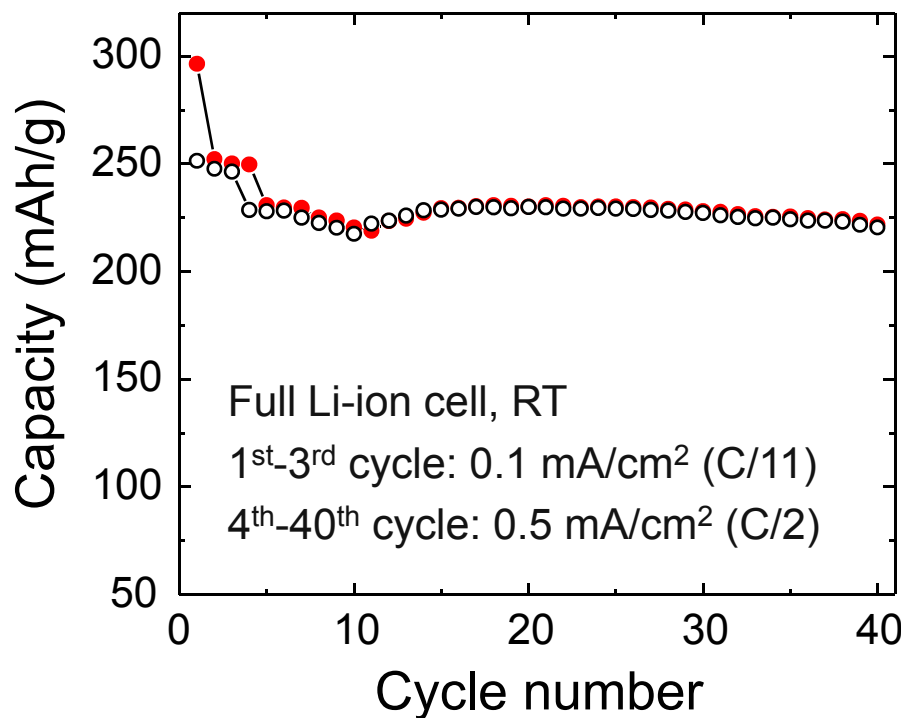
(0.5Li<sub>2</sub>MnO<sub>3</sub>•0.5LiNi<sub>0.44</sub>Co<sub>0.25</sub>Mn<sub>0.31</sub>O<sub>2</sub> electrodes in Li half cells)



- Li-Ni-PO<sub>4</sub>-treated electrodes show stable cycling at various rates
- Surface-treated electrodes show superior cycling efficiency  
⇒ suppression of electrode-electrolyte reactions at 4.6 V?

# Cycling stability of a Li<sup>+</sup>-ion cell

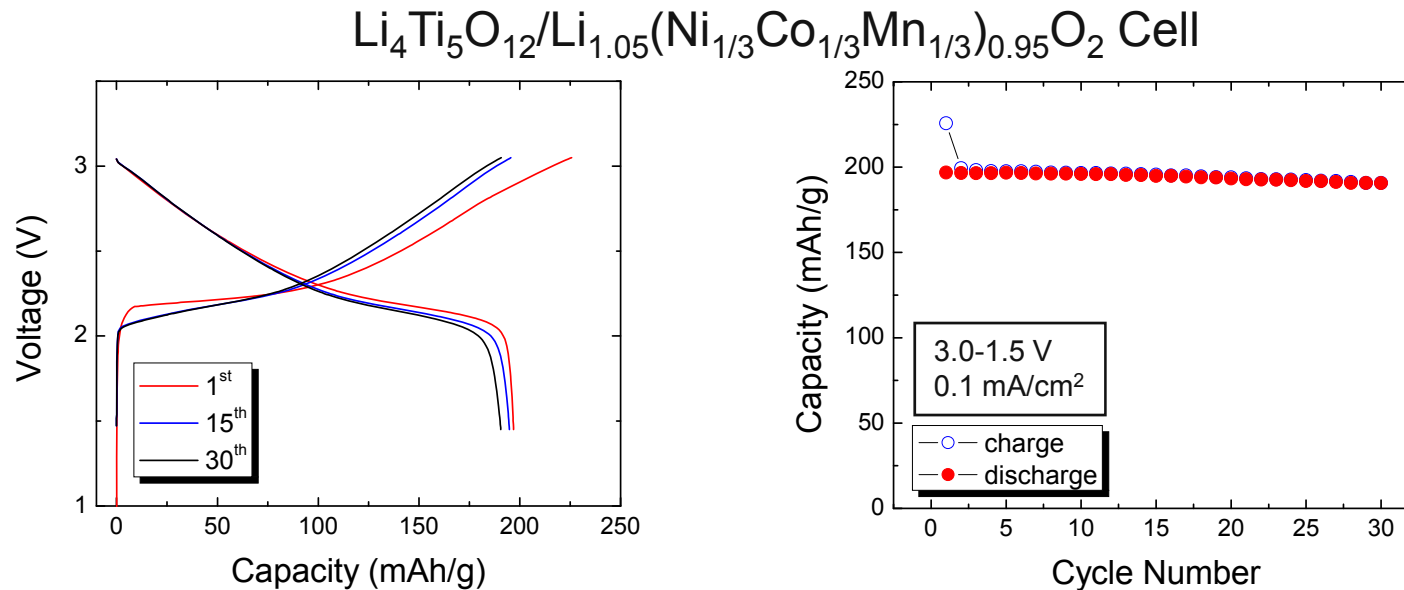
(Li-Ni-PO<sub>4</sub> treated 0.5Li<sub>2</sub>MnO<sub>3</sub>•0.5LiNi<sub>0.44</sub>Co<sub>0.25</sub>Mn<sub>0.31</sub>O<sub>2</sub> electrode)



- Li-ion cell data (MAG-10 anode) validate the half-cell data
- The electrodes deliver 225 mAh/g at a C/2 rate at RT
- Compositional and electrochemical performance optimization in progress

# Other Applications: $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ Electrodes

- The utility of  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$  cathodes was demonstrated in other Li-ion cell configurations:
  - blended with spinel to compensate for rate limitations (Commercialized; U.S. Pat. 7,303,840 (2007)).
  - with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anodes in 3.0-2.0 V cells



- ❖ 190-200 mAh/g from  $0.1\text{Li}_2\text{MnO}_3 \bullet 0.9\text{LiMn}_{0.256}\text{Ni}_{0.372}\text{Co}_{0.372}\text{O}_2$
- ❖ 240 mAh/g from  $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiMn}_{0.31}\text{Ni}_{0.44}\text{Co}_{0.25}\text{O}_2$  (fluorinated)

# Theoretical Modeling of Surface Structures and Electrochemical Phenomena

- Studies motivated by the necessity to understand solubility of metal oxide cathodes and their instability at high potentials
- Initial studies on  $\text{H}^+$ - $\text{Li}^+$  ion exchange phenomena in  $\text{LiCoO}_2$  (BATT Review 2008)
- Current studies on solubility and surface structure of  $\text{LiMn}_2\text{O}_4$
- $2 \text{LiMn}_2\text{O}_4 + 4 \text{H}^+ \rightarrow 3 \lambda\text{-MnO}_2 + \text{Mn}^{2+} + 2 \text{Li}^+ + 2 \text{H}_2\text{O}$  (Hunter, 1981)
  - Calculate *Hunter-dissolution-reaction* free energy  
 $\Rightarrow$  Pourbaix-like phase diagram
  - Disproportionation reaction - *No bulk  $\text{Mn}^{2+}$ , anion neglected*
  - Model  $\text{LiMn}_2\text{O}_4$  - (111) free surface atomic structure
  - Model  $\text{LiMn}_2\text{O}_4$  - (111)/ $\text{H}_2\text{O}$  interface structure (in progress)

# Calculation of $\Delta G$ (Dissolution) for $\text{LiMn}_2\text{O}_4$

Solids - GGA+U (VASP)

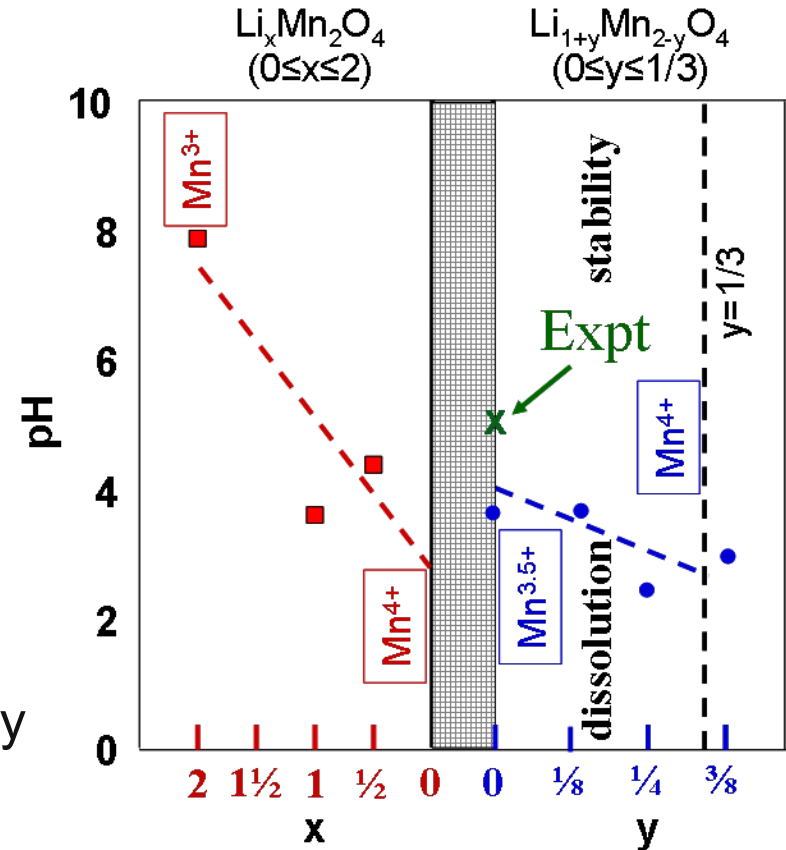
$$G(T) = G_{\text{static}}(T=0) + G_{\text{vibrational}}(T)$$

Aqueous Ions

$$G_{\text{aq}} = \underset{\text{GGA}}{G_{\text{atom}}} + \underset{\text{EXPT}}{G_{\text{ionization}}} + \underset{\text{EXPT}}{G_{\text{hydration}}}$$

- Calculated phase diagram consistent with experimentally observed solubility trends of  $\text{Mn}^{3+}$  in acidic electrolytes (disproportionation) and in  $\text{Zn}/\text{MnO}_2$  alkaline cells.

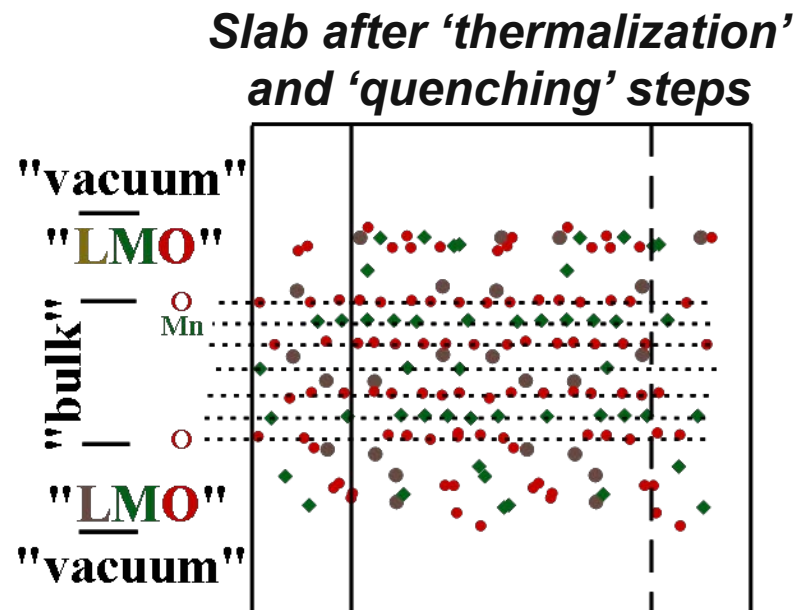
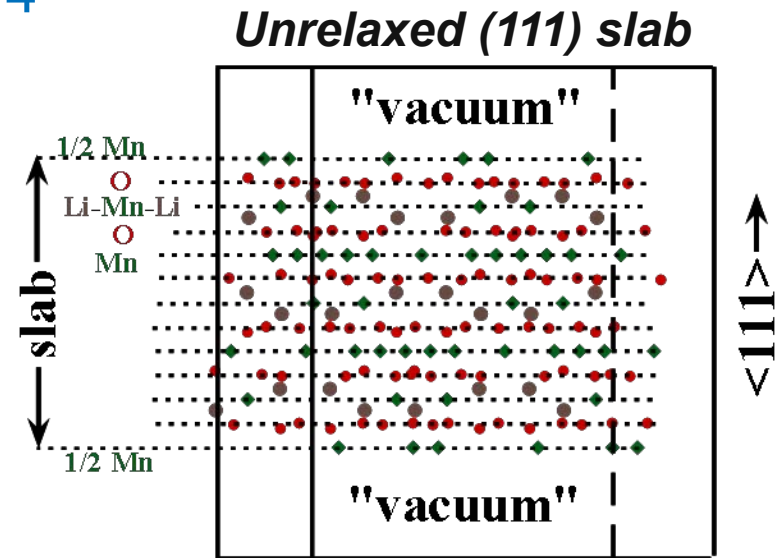
Spinel Dissolution Phase Diagram



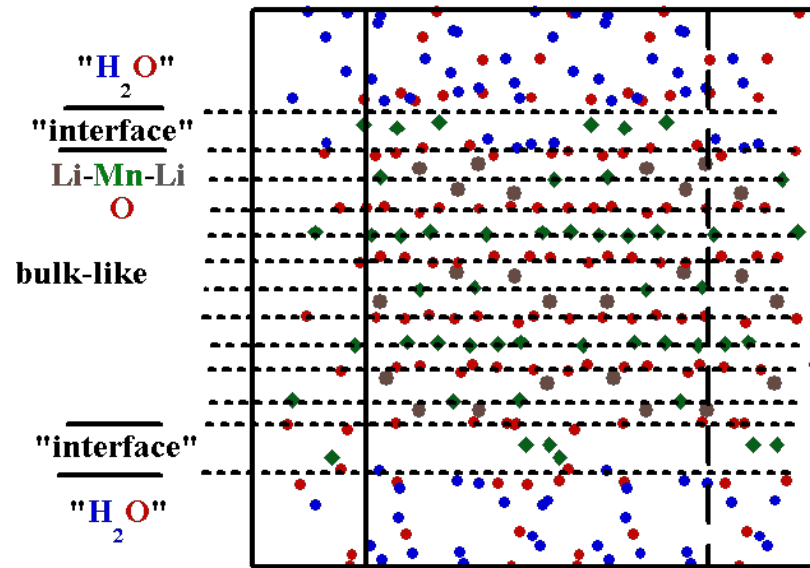


# Modeling $\text{LiMn}_2\text{O}_4$ Surfaces

- Layers pure for (111) orientation:  
... | 3Mn | 4O | Li | Mn | Li | 4O | ...
- Treat Mn-terminated slab (84 atoms)
- Slab dimensions  $\sim 12 \times 10 \times 25 \text{ \AA}$
- Model surface reconstruction:  
Mn site occupancy = 0.5  
on termination layers



# (111) $\text{LiMn}_2\text{O}_4$ / $\text{H}_2\text{O}$ Interface



## Preliminary Conclusions:

- O atoms rearrange to encapsulate under-coordinated Mn ions
- Li atoms drawn in wake of O to maintain neutrality  
⇒ 3 top layers form "mixed" Li-Mn-O at free surface
- Mn coordination no.  $\sim 4$  at Mn-terminated (111) free surface
- Mn coordination no.  $\sim 5$  at (111)  $\text{LiMn}_2\text{O}_4$  /  $\text{H}_2\text{O}$  interface
- Mn oxidation state  $\sim 3+$  at free surface or  $\text{H}_2\text{O}$  interface

# Future Work - FY2009/FY2010

- Continue to exploit and optimize  $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$  electrodes (composition and performance) with the particular goal of reaching or exceeding the energy and power goals required for 40-mile PHEVs and EVs.
- Focus on surface studies: fluorides, phosphates – use both experimental techniques and theoretical modeling that will lead to an improved stability and rate capability of metal oxide electrodes at high potentials – continue existing, unfinished thrusts in projects (surface structure analysis, modeling and prediction).
- Explore synthesis routes to fabricate novel cathode materials and architectures or improve existing ones. (New, proprietary technique shows promise).

# Summary

- Progress was made in stabilizing the surface, and improving the rate capability of high-capacity  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  electrodes (M=Mn, Ni, Co) when charged to a high potential (4.6 V).
- Rechargeable 200 mAh/g obtained at C/1 rate
- $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  electrode materials are now also under investigation in the ABRT program and have the attention of industry
- The approach adopted opens the door to new stabilizing surface structures and for further performance improvements – future work.
- Theoretical modeling was used to complement experiment to understand, and provide direction for designing, stabilized surfaces – future work.
- Preliminary results show that a new (proprietary) synthesis technique shows promise for fabricating electrode materials with modified morphologies and electrochemical properties – future work.

## Acknowledgment

Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged - David Howell